The Pennsylvania State University

The Graduate School

Department of Civil and Environmental Engineering

TESTING SOILS FOR PETROLEUM CONTAMINATION:

ANALYSIS OF TECHNIQUES AND RESULTS

A Report in

Environmental Engineering

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Engineering

December 1995

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ABSTRACT

Techniques used for the testing of soils for petroleum contamination were researched. The focus was on the probable accuracy of the petroleum content data and the possible problems resulting from the testing techniques utilized. General information regarding petroleum in soil environments and methods of obtaining soil samples was included provided to support the discussion. Laboratory and field methods for measuring petroleum contamination in soils were included with an emphasis on the accuracy of the data obtained. Information concerning quality assurance of soil sampling data was included to assist in assessing ongoing soil investigations. Two sets of data from soil investigations under the direction of the U.S. Army Corps of Engineers, Engineer District Europe were reviewed.

A major issue facing the U.S. Army Corps of Engineers is cleanup of military installations throughout the world. Much of the contamination is due to the massive use of petroleum products by the military. Contractors are utilized to investigate possible petroleum product contamination and often the data provided is not thoroughly clear. A better understanding of the techniques available for testing soils for petroleum product contamination could facilitate clarity of data provided and decisions regarding the sites.

There is a need for further research in the area of testing soils for petroleum product contamination. The complexity of petroleum products makes the subject a formidable challenge. Additives, a wide range of physical properties, and the numerous chemical classes in petroleum products compound the problem.

Sample collection and preservation are a vital part of the process. Analysis of soil itself or the soil gas are the two basic approaches for determining petroleum product contamination levels. Although the mechanics of the sampling procedure affect the data obtained very little if applied uniformly, there are several vital aspects of the process. Testing must be conducted rapidly after sampling to negate possible biodegradation and chemical changes in samples. Due to the volatile nature of most petroleum products, measures must be taken to minimize their escape. Samples must be kept at near water freezing temperatures to maintain their integrity. Both case studies failed to provide specific information regarding these critical aspects of their sampling programs, raising questions about the data they provided.

Most laboratory techniques are derived from EPA testing methods that were not designed for the purpose. Gas chromatography coupled with mass spectrometry, photoionization detectors, or flame ionization detectors currently provide the most accurate data but have weaknesses which should be considered when reviewing results. One of the case studies utilized gas chromatography alone to test some of the samples.

Field techniques are not currently regarded as an acceptable replacement for laboratory techniques by most regulatory agencies but are growing in acceptance. There are advantages of field testing over laboratory testing such as immediate results and alleviation of potential volatile losses. The advantages of field testing have made it a more desirable target for current research. Portable laboratory equipment can provide field results much like those obtained in the laboratory but are still in an infancy stage with respect to dependability and durability. Immunoassays are proven to provide good

field test results but sometimes require a level of competence and understanding that is often above existing levels. Prototype field techniques such as laser-induced fluorescence and fiber-optic chemical sensors are continuing to improve and should be viable options for field testing and screening in the near future. Both case studies utilized field techniques with marginal success. The immunoassays were newly introduced and operator competence may have affected results. The portable photoionization detector testing procedure was not properly outlined in the investigation report leaving room for doubt of data obtained.

Quality assurance is important to testing soils for petroleum product contamination. Utilizing the EPA's recommended Data Quality Indicators for developing a sampling plan and evaluation of the data obtained is recommended. Both case studies either failed to indicated their full quality assurance measures or failed to sufficiently utilize them.

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ACKNOWLEDGMENTS

Thanks go out to many at P.S.U.:

> My advisor Dr. Raymond W. Regan for your support and confidence in times of need.
>
> The cage crew who gave motivation and academic assistance without hesitation.
>
> The entire department for the "climate" that encourages old students like me to participate and contribute.

ESSAYONS to all the other Army, Navy, Air Force and even Marine students!

Thanks to the Environmental people at EDE for providing me with a challenging report subject and some data to make it work.

To my wife Beate, thanks for your patience and support. It may be obvious to me but it cannot go "without saying" - I could not have done it without you.

Chapter 1

INTRODUCTION

1.1 STATEMENT OF PROBLEM

One of the major issues facing the U.S. Army Corps of Engineers (Corps) is the cleanup of military installations in the continental United States and abroad. Due to the preponderance of vehicles and equipment in the military, petroleum products are one of the major contaminants. Some bad practices in the past as well as accidents have contaminated the soil with products ranging from jet fuel to marine diesel fuel.

An assessment of a contaminated site requires testing and characterization of the soil contamination. In order to plan and carry out effective remediation of petroleum contaminated soils it is necessary to define the source of the contaminant and the subsurface distribution. The U.S. Environmental Protection Agency (EPA) has developed numerous laboratory methods for characterizing petroleum product contamination but has done little with field techniques. There is no definitive guidance on what tests should be run on soils thought to be contaminated with petroleum products.

A lack of organic resources and laboratories forces the Corps to use various contractors and private laboratories to conduct soil investigations and contaminant characterization. The contractors and laboratories utilize a variety of methods that include laboratory tests as well as field analysis. There has been discussion, and

sometimes disagreement, on which tests are more accurate and dependable, and what the test results truly indicate.

1.2 OBJECTIVES

The primary objective of this report is to provide a document which can serve as a reference when dealing with soil testing for petroleum product contamination. This document is meant to be a primer on the current state-of-the-art techniques and their strengths and weaknesses.

Specific objectives include:

a. Provide an overview of the techniques available, both laboratory and field, for testing of soils for petroleum contamination. Discuss frequently used methods and some of the more experimental methods available.

b. Provide pros and cons of the various techniques and a comparison of the laboratory and on-site tests. Furnish information regarding the accuracy of the test results.

c. Briefly discuss basic requirements for Quality Assurance within a soil testing program. Provide a simple method for evaluating a testing program's Quality Assurance.

d. Analyze soil investigation data from two ongoing projects within the auspices of the Corps' Engineer District, Europe (EDE). Provide some insight as to the quality of the data; the probable accuracy and possible shortcomings.

1.3 RATIONALE

The ultimate cost of site remediation is strongly influenced by the number of soil samples and tests needed for site assessment and characterization. The choice of a certain soil testing method or technique could greatly reduce expenses by reducing the number of additional tests required or by facilitating the optimum placement of measurement locations. Some test methods, being much more rapid than others, could greatly decrease the time required to assess and characterize, therefore reducing the time required to remediate a site.

The information in this report should assist understanding the techniques available for detecting petroleum product contamination in soil as well as the data provided by those techniques. It may assist in decisions regarding requirements for contractors and laboratories investigating sites. It may provide some help with decisions about the future of some sites under investigation.

Various products are mentioned in this engineering report, especially in areas concerned with newer technologies. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1.4 BACKGROUND

As a Captain in the U.S. Army Corps of Engineers, I will serve a utilization tour as an environmental engineer within EDE. I obtained data from two soil investigations in different ongoing projects in EDE:

a. Hardstand #72: Performed by HYDRODATA GmbH on a site in Camp Albertshof, Hohenfels Training Area, Germany in November and December of 1994. The purpose of the investigation was to complete the investigations begun in 1992 and 1993 to determine the petroleum product contamination to the soils in the area of the designated hardstand. A hardstand is a series of reinforced concrete slabs with sealed joints on which heavy vehicles (i.e. tanks) are parked and maintained. Facilities for maintenance and refueling routinely exist on hardstands. The investigated area was level and mostly sealed with concrete or asphalt, covering approximately 400 m^2.

b. Phase III Soil and Groundwater Investigation, Sludge Landfill: Performed by Dames & Moore GmbH & Co. in Grafenwohr Training Area, Germany. The purpose of this investigation was to conduct a follow-up soil and groundwater contamination assessment at five individual locations throughout the training area. Area 2, the Oil Loading Station, was chosen for this report because it was purely a soil investigation. It consisted of testing the soils in and around a small concrete loading area located near the railroad tracks on which oil was on-loaded and off-loaded from tanker cars. Although the main goal of this investigation was to determine lead contamination, soil samples were also screened for petroleum product contamination.

Much of the information within this engineering report was taken from the above reports of investigation and used as a basis for discussion and analysis. However, all analysis and conclusions are the work of the author.

This Engineering Report will be delivered to the Commander, U.S. Army Engineer District, Europe for analysis, comparison, and consideration in future projects requiring testing of soil for petroleum product contamination.

Chapter 2

PETROLEUM CONTAMINATION IN SOILS

2.1 INTRODUCTION

Analysis of petroleum product residue in soil can be a formidable challenge. The following is a list of a few factors that make this so:

- Petroleum products are often blended with various additives to meet certain criteria. The result is that the final products have little resemblance to the initial crude oil. Table 1 provides a summary of product types produced from petroleum.
- Most petroleum products are exceptionally complex materials with a wide range of physical properties. They may contain hundreds or thousands of constituents with boiling point distributions on the order of hundreds of degrees Celsius.
- Several chemical classes are usually represented by the hydrocarbon types in petroleum products. Paraffin's, olefins, aromatics, heteroaromatics, and various polar hydrocarbons containing Oxygen, Nitrogen, and Sulfur can be present. Table 2 provides a summary of hydrocarbon types in petroleum.

To better understand some of the discussions within this document, it is best to review some of the aspects of petroleum contamination in soils. This chapter briefly reviews some of the more important aspects of petroleum product chemistry and contamination measurement.

Table 1: Summary of Product Types Produced from Petroleum

Number of Carbon Atoms	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	$>C_{20}$
Boiling Point of Normal Paraffin at 760 mm Hg																					
°C	−161	−89	−42	−0.5	+36	69	98	126	151	174	196	216	235	253	270	287	302	316	329	343	
°F	−259	−127	−44	+31	97	156	209	258	303	345	384	421	456	488	519	548	575	601	625	649	
Refinery off gas																					
Liquefied petroleum gas																					
Butanes/butylenes																					
Ligroine (naphtha solvent)																					
Precipitation naphtha (solvent)																					
V.M. & P. naphtha (solvent)																					
Mineral spirits																					
Cracking naphtha																					
Reformate																					
Gasoline																					
Kerosine, diesel fuel																					
Aviation turbine fuel																					
Gas oil, fuel oil																					
Transformer oil																					
FCC & hydrocracker feed																					
Lubricating oil																					
Asphalt, pitch																					
Wax																					
Residuums & asphalt																				C_{44}^{+}	

SOURCE: Drews (1990)

Table 2: Summary of Hydrocarbon Types in Petroleum Fractions

Number of Carbon Atoms	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	$>C_{20}$
Boiling Point of Normal Paraffin at 760 mm Hg																					
°C	−161	−89	−42	−0.5	+36	69	98	126	151	174	196	216	235	253	270	287	302	316	329	343	>355
°F	−259	−127	−44	+31	97	156	209	258	303	345	384	421	456	488	519	548	575	601	625	649	>671
Normal alkanes	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Branched alkanes	—	—	—	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Cycloalkanes, mono-	—	—	—	—	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Cycloalkanes, di-	—	—	—	—	—	—	—	M	P	P	P	P	P	P	P	P	P	P	P	P	P
Cycloalkanes, poly-	—	—	—	—	—	—	—	—	—	—	—	—	M	P	P	P	P	P	P	P	P
Noncyclic alkenes	—	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC
Cycloalkenes	—	—	—	—	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC	PC
Alkylaromatics, mononuclear	—	—	—	—	—	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
Alkylaromatics, dinuclear	—	—	—	—	—	—	—	—	—	P	P	P	P	P	P	P	P	P	P	P	P
Alkylaromatics, polynuclear	—	—	—	—	—	—	—	—	—	—	—	—	—	M	P	P	P	P	P	P	P
Cyclanoaromatics, mononuclear	—	—	—	—	—	—	—	—	P	P	P	P	P	P	P	P	P	P	P	P	P
Cyclanoaromatics, dinuclear	—												P	P	P	P	P	P	P	P	P
Cyclanoaromatics, polynuclear	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	P	P	P	P	P
Acetylenes	—	P[a]	P[a]	P[a]																	
Heterocyclics	—	—	—	—	M[b]	M[b]	M	M	M	M	M	M	M	M	M	P	P	P	P	P	P

P = Present in major amount.
M = Present in minor amount.
PC = Present in cracked products only.
P[a] = Acetylenes are found only in gases and liquids subjected to high temperature.
M[b] = Thiophene is usually found in the C_6 fraction.

SOURCE: Drews (1990)

2.2 PETROLEUM PRODUCT CHEMISTRY

Petroleum product composition can change dramatically after release into the environment. Volatilization, dissolution and degradation can be responsible for this. To simplify the problem, it may be best to look at what soil and petroleum consist of separately and then look at them together. Uncontaminated soil is a three phase system of solids, water, and air. The soil solids are predominately minerals such as silica or calcite and organic matter. Petroleum products are basically composed of a complex mixture of hydrocarbons. Hydrocarbons do not interact well with the minerals in soil. Therefore, it can be helpful to think of soil with respect to petroleum product contamination as and inert mineral phase, organic matter, water, and air with the contaminant not affecting the mineral phase (Denahan et al. 1990, p. 99).

It follows that to look for petroleum contamination in soils, one must check the soil's air (soil gas), water, or organic matter. The relative amounts of contaminants in vapor form, dissolved in water, or sorbed to solids depend solely on the petroleum product physical chemical properties and the relative amounts of each of these phases in the soil. The petroleum is assumed to distribute itself among these phases so as to establish an equilibrium. Various models exist that can be applied to petroleum hydrocarbons. With knowledge of the contaminant concentration in any of the phases, the concentrations in the other phases can be estimated.

It is important to look closely at the effects of petroleum product aging in the soil environment. The weathering process is very complex and not very predictable and the extreme volatility of some petroleum components require special consideration.

When interpreting results from monitoring of the air phase of soils, one must recognize that the vapor "signal" of petroleum products may fade and that the relationship between the soil gas and the other phases may steadily change.

Almost all methods for detecting petroleum contamination include analysis for benzene, toluene, ethylbenzene and xylenes (BTEX) and total petroleum hydrocarbons (TPH). BTEX is normally targeted as the constituent of greatest concern because it has high water-solubility, volatility, and toxicity. TPH analysis has been divided into three categories defined by differences in boiling points:

1. TPH I -- low to medium boiling point fuels, including the full range of gasoline and some military jet fuel (C4-C12).
2. TPH II -- medium to high boiling point fuels, including kerosene, fuel oil #2, diesel, and commercial-grade jet fuel (C9-C16).
3. TPH III -- other petroleum products, including residual fuel oils, lubricating and cutting oils, hydraulic fluids, and greases (C13-C20).

Table 1 provides an indication of what product types exist in each category.

2.3 UNITS OF MEASUREMENT

Petroleum contamination in soils is measured in the three phase system of solids, liquid, and air. The basics for measurement in the different media are not the same. This causes occasional confusion regarding the units and conversions. The following provides some basics which should help alleviate possible misunderstandings.

Contaminant concentrations in solids are most commonly expressed on a mass/mass basis. For most laboratory procedures, soil samples are weighed at field moisture then extracted to determine the mass of contaminant in soil, liquid, and gas phases. Moisture content is determined and the total mass of contaminant is referenced to the mass of dry soil. Contaminant concentrations are normally expressed as ug/g or mg/kg or ppm by weight.

Contaminant concentrations in water are commonly reported on a mass/volume basis, as mg/L. Specific gravity of water (1 L is approximately = 1 kg) links mass and volume scales. Consequently, concentration expressed in mg/L is nearly equivalent to concentrations in mg/kg. Therefore, either can be reported as ppm.

Bulk density of most soils is 1.5 - 2.0 kg/L. This is not far off from the specific gravity of water. This makes it possible, without great error, to compare soil contaminant concentrations to water contaminant concentrations without considering the difference between mass/mass and mass/volume (Denahan et al. 1990, p. 99).

Contamination concentrations in the air phase are measured in the soil gas. These concentrations cannot be looked upon as easily as those for water and solids. Standard reporting for vapor phase concentrations is volume/volume. This is equal to moles/moles based on the Ideal Gas Law. Therefore, 1 ppm of contaminant in the air is equal to 1 uL/L or 1 micromole of contaminant/1 mole of air. To convert from contaminant concentrations in air as ppm by volume to a mass/volume basis, the molecular weight of the contaminant must be considered. Using benzene as an example:

MW = 78 gm, occupies 22.4 L at standard temperature and pressure

density of pure benzene vapor (at STP) = 78 gm/22400 mL = 3.5×10^{-3} gm/mL

Therefore, if benzene concentration in air = 1 ppm

then concentration on mass/volume basis = 3.5 ug benzene/L of air.

Generally, soil concentrations of petroleum hydrocarbons expressed in ppm (mass/mass) will be substantially less than soil gas concentrations in ppm (volume/volume).

2.4 APPROACHES TO MEASUREMENT

Analysis required to evaluate petroleum product releases into soil take a variety of forms. Analytical objectives are diverse and often poorly specified. They range from a simple assessment of "presence or absence" to determination of the concentration of certain toxic substances these products contain. The least specific and most general analytical approach usually involves some form of TPH measurement but there are those that focus on target compounds such as BTEX.

The EPA has developed some commonly used analytical measurement methods which have origins in the techniques specified for monitoring. Examples include using headspace or purge and trap with gas chromatography (GC) techniques for the full range of gasoline (C4-C23) and using sonication extraction with GC techniques for diesel motor fuels (C9-C22) and kerosene (C10-C16). These techniques will be discussed later in this report. It is important to note that most of the EPA methods were not specifically developed for, nor have they been systematically evaluated for, analysis of petroleum products in soil. There is a need for further work in this area (Potter 1989, p.97).

Petroleum products are perhaps best suited for vapor phase analysis because of the significant component of volatiles in their makeup. Whenever petroleum products are released into soil, a vapor phase component will be present. As mentioned earlier, with vapor phase analysis, it is important to consider the effects of aging and weathering on the petroleum product phases.

Chapter 3

SAMPLE COLLECTION AND PRESERVATION

3.1 INTRODUCTION

Sample collection and preservation are keys to a good measurement program. Actions taken initially to collect and preserve the soil samples can significantly impact on the results obtained during analysis. Two basics approaches exist for gathering samples to test for petroleum contamination: gathering soil samples and gathering soil gas samples. Either type of sample can be examined in the laboratory or the field. Collection techniques are believed to have a significant effect on test results but have received little attention from regulators (Klopp and Turriff 1994, p.141).

Preservation of a soil sample is perhaps the most likely portion of the measurement process to cause a bias or problem with the data obtained. This is especially true due to the volatile nature of many of the compounds in petroleum products.

Blanks provide a way to measure the success of the sample collection and preservation as far as preventing contamination. Their use is critical to the ability to assess and control sample contamination.

This chapter discusses soil sample collection and preservation techniques which are commonly used as well as some basics in the use of blanks to control contamination.

3.2 SOIL COLLECTION

There is little information on the efficiencies and expectations of techniques used for soil collection. It is difficult to draw conclusions about the performance of soil collection techniques because the heterogeneity of the soil matrix makes comparing even collocated samples difficult. The problem is compounded by the difficulty of recreating the following field conditions in the laboratory:

- Contaminant compositions derived from natural weathering of the petroleum.
- The adsorption and molecular interactions that occur over time.
- Natural bacterial populations that have adapted to the type and concentration of the petroleum.

Testing for soil contamination requires one of two basic techniques when gathering the soil. One consist of taking an undisturbed sample and quickly isolating it from ambient conditions. The sample should be sealed into a container with minimal or no headspace, chilled, and, depending on whether it is a laboratory test, taken to the laboratory (Denaham et al. 1990, p. 98). The other is to immerse the sample in methanol immediately after collection. The goal of both techniques is to eliminated losses of volatiles from the soil.

There are numerous devices which can be used to physically gather soil samples. The following is a list of a few of the more commonly used devices:

- ENCORE sampler: A stainless steel cylindrical coring device equipped with a plunger. The chamber is flanked by o-ring seals located behind the plunger face and in the cap.

- Brass Tube: A cylindrical brass tube with plastic end caps that are sleeved with Teflon sheets.
- Spatula: A common laboratory stainless steel scoop type.
- Graef, Anhalt, Schloemer (GAS) Sampler: A stainless steel cylindrical coring device equipped with a handle.
- Soil Syringe: Common laboratory 25 mL disposable syringe with the end cut off.

Klopp and Turriff (1994) did a series of experiments using the devices above and found that as long as the samplers were properly used and the samples were rapidly taken and preserved with methanol, the device used does not appear to matter. If the soil samples remain in the devices too long (over two hours), there can be a significant loss of volatiles. The soil syringe and the GAS sampler in particular were shown not adequate for any type of storage (p. 148).

Often, soil samples are obtained from the core barrels of drilling devices when the sample must be obtained from greater depths. Percussion drills and Sondier boring devices can be used in such cases. The soil sample is taken from the core and placed in sample containers.

3.3 SOIL GAS

Methods for sampling and analyzing vapor phase components of petroleum contamination can be divided into two broad categories:

1. In situ methods -- There is no need of a soil sample. Two primary variations:

a. Active -- A sample of vapor is extracted from the vadose zone by means of a hollow probe and a vacuum pump. Can utilize the soil gas itself for analysis or analyze what is adsorbed onto a medium within the probe.

b. Passive -- A collection device containing an absorbent medium is buried in the soil and exhumed after a specific period of time.

2. Headspace -- Requires the collection of a soil sample from which the vapor phase components are measured from the space directly above the soil.

For the active soil gas probe sampling procedure, probes are hammered 1.3 m into the ground. A sampling manifold is then attached and gas is drawn though the sampling assembly into a 1 L sample bag by a gas pump. A first bag is used to purge the assembly. Subsamples can be withdrawn from the sampling manifold with gas-tight syringes for analysis (Kerfoot 1987, p. 1023). Figure 1 depicts a typical configuration of this device.

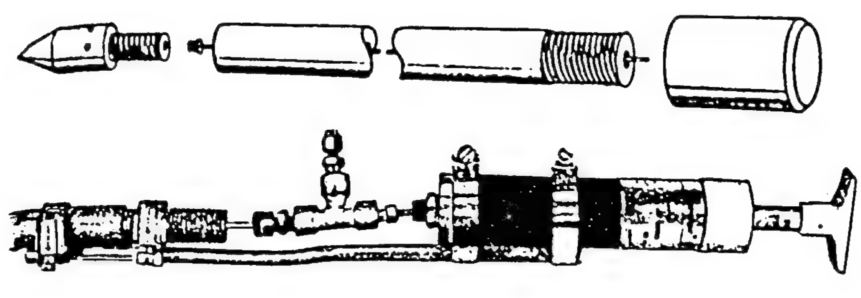


Figure 1: Sampling Probe (top) and Manifold Attached to Probe (bottom)
SOURCE: Kerfoot (1987)

Dynamic trapping is another active method of sampling soil gases for laboratory analysis. It relies on evacuating soil gas for 15 minutes at 100 cm^3/min through a probe containing a medium of activated charcoal. After the gas is evacuated the samples are sealed and transported to a lab for analysis using EPA Method 602 (Denaham et al. 1990, p. 97).

The passive techniques may utilize activated charcoal as the absorbent medium. They have several disadvantages and are not often utilized. They rely on the natural flux of the vapor phases which is often slow and variable. To achieve desired results, it may be necessary to use the technique two or more times.

Headspace measurements require filling jars 1/2 full with a soil sample, sealing the jar with aluminum foil. The jar is then agitated and allowed to equilibrate for 5 - 10 minutes. The foil is then punctured by a probe or a sample is withdrawn using a syringe to measure the vapor phase hydrocarbons. Fizgerald (1989) found that better results are obtained when 16 ounce jars are used (comparing 16, 9, and 5 ounce jars) and filled to 1/2 capacity. The shape of the jars or the temperature did not significantly affect test results (p. 135).

3.4 STANDARD PRESERVATION TECHNIQUES

Samples are preserved to prevent any chemical change that might take place between the time the sample is taken and the time it is analyzed. There are no prescribed preservation techniques for soil samples for organic or inorganic analysis. There are a few practices that are widely accepted: seal sample containers, minimize headspace,

refrigerate samples during storage and transportation, and analysis of the samples as soon as possible (Keith 1988, p. 411).

Sealing samples and minimizing headspace will minimize the loss of volatile compounds, and minimize the possibility of aerobic biodegradation or chemical oxidation effects.

Storing samples at reduced temperatures can slow both volatilization and biodegradation of the sample. The standard temperature of ice (about 4 °C) is probably the most reasonable to use. Anything lower would further reduce volatilization and biodegradation but might adversely affect the sample by freezing any water within it.

The need to expedite analysis can not be overstated. Other than slowing reactions occurring within the sample by utilizing the techniques explained above, there is no way to preserve the sample. Normally, if the analysis method requires an extraction or digestion, it is best to carry out this step as soon as possible. Consistency is a necessity for the times between sample collection and analysis including the method used to carry out the extraction or digestion. Without it, there is no easy way to predict what kind of bias may be part of the results.

The most difficult problem experienced with analyzing contaminated soil samples is obtaining reliable analytical results for volatile compounds. Preservation of the volatiles in the samples represents a particular problem that often creates bias in data. Keith (1988) concluded from a field investigation of the Petro-Processors site that the full sampling process, completely through the laboratory sub-sampling, obtains better volatile results when planned such that the analysis technique utilizes a larger sample.

For example, with all other conditions equal, methods that utilize 4 gm of sample provide more accurate results than those that utilize only a few tenths of a gram of the sample (p. 412).

3.5 BLANKS

Blanks are essential samples having negligible or unmeasurable amounts of the contaminant of interest. They intentionally do not contain the substance of interest but are, in all other respects, the same as the actual samples. They are essential to analytical studies because they make it possible to adjust results to compensate for the effects of contamination.

Table 3 provides a summary of the types of blanks often used in environmental measurements. There are generalized rules for the frequency of use for each type of blank but often experience and intuition play a large role in determining when to utilize them (Keith 1988, p. 127).

Control charts provide the most effective mechanism for interpreting blank results. They can be used to detect changes in the average background contamination of a system. Any new source of contamination would show up if the control charts are used properly.

Table 3: Summary of Blank Types

Common Name	*Other Names*	*Uses*	*Description*
		Laboratory blanks	
System blank	Instrument blank	To establish baseline response of an analytical system in the absence of a sample	Not a simulated sample but a measure of instrument or system background response
Solvent blank	Calibration blank	To detect and quantitate solvent impurities; the calibration standard corresponds to zero analyte concentration	Consists only of the solvent used to dilute the sample
Reagent blank	Method blank	To detect and quantitate contamination introduced during sample preparation and analysis	Contains all reagents used in sample preparation and analysis and is carried through the complete analytical procedure
		Field blanks	
Matched-matrix blank		To detect and quantitate contamination introduced during sample collection, handling, storage, transport, preparation, and analysis	Made to simulate the sample matrix and carried through the entire sample collection, handling, and analysis process
Sampling media blank	Trip blank	To detect contamination associated with sampling media such as filters, traps, and sample bottles	Consists of the sampling media used for sample collection
Equipment blank		To determine types of contaminants that may have been introduced through contact with sampling equipment; also to verify the effectiveness of cleaning procedures	Prepared by collecting water or solvents used to rinse sampling equipment

SOURCE: Keith (1988)

Chapter 4

LABORATORY TECHNIQUES

4.1 INTRODUCTION

This chapter is an overview of the type of tests and test procedures use in laboratories to detect petroleum contamination on soils. There numerous techniques that are used, sometimes relying on sophisticated equipment. Many of the techniques are based on existing or modified EPA methods.

4.2 IR AND GRAVIMETRIC METHODS

EPA methods for determination of TPH using infrared spectroscopy (IR) and gravimetric means include Method 418.1 "Total Recoverable Petroleum Hydrocarbons" and Method 413.1 "Oil and Grease". Both methods involve extraction of hydrocarbon residue using an organic solvent or solvent mixture. After extraction, the sample is concentrated using rotary thin film evaporation or other techniques.

For Method 418.1, IR absorbency of freon-extracted hydrocarbons relative to a mixed calibration of chlorobenzene, iso-octane, and n-hexadecane is measured. Wavelengths in the 3200-2700 wave number range reflect absorption of vibrational energy by carbon to hydrogen bonds. The concentration is expressed relative to the standard mixture (Potter 1989, p. 99).

Method 413.1 gravimetrically determines the total hydrocarbon content. The solvent is completely evaporated and the residue is weighed. Although procedures used

vary widely, gravimetric methods are often used for TPH III investigations (Chang 1992, p. 240).

Advantages to these methods include the modest costs to conduct them and the fact that extensive technical training is not required to conduct them.

Disadvantages include a wide variance of precision and accuracy depending on the weathering of the products involved and the possibility of significant volatile loss in the solvent concentration step. Additionally, with Method 418.1 there is a problem with heavier petroleum products such as residual fuels in that their constituents are poorly soluble in freon (Potter 1989, p. 105).

4.3 GC-MS

Perhaps the most well known and most frequently used method for analysis utilizes gas chromatography (GC) coupled with mass spectrometry (MS). Currently, GC-MS methods are the only methods that can measure all volatile and semivolatile compounds in petroleum products. One of the most utilized methods is EPA Method 624.

A chromatographic system basically separates substances. It consists of two phases: a mobile phase that streams over a stationary phase. The substances to be separated have different relative affinities for the stationary and the mobile phases. Thus, the substance with the relatively higher affinity for the stationary phase moves with a lower velocity through the chromatographic system than the substance with the

lower affinity. This difference in velocity ultimately leads to physical separation of the components in the sample (Jonsson 1987, p. 3).

The MS is an electronic, high-vacuum instrument used for analysis of gases, liquids or volatilized solids by means of the dissociation of molecules by electron impact, chemical ionization, or field ionization bombardment and the subsequent separation of the positive ions according to their mass-to-charge ratio (Gudzinowicz et al. 1976, p. 2). When coupled with a GC, the MS can provide data on the petroleum product compounds within a sample.

Some of the limitations of the GC-MS methods follow:

- Sample workup is critical, more so than with other methods. Results dependent on the efficiency of the solvent used in extraction.
- Accuracy is of particular concern due to the fact that an abundance of one type of contaminant compound can "clog" a test.
- Require high level of competence and experience. Results are very dependent on the experience of the analyst in identifying and quantifying the detected compounds.

4.4 GC WITH PID OR FID

One of the state of the art techniques used for detecting petroleum contamination is gas chromotography (GC) for separation with a photoionization detector (PID) or a flame ionization detector (FID). EPA 500, 600, and 8000 series methods are probably the most widely used methods for direct measurement of specific constituents in

petroleum contaminated soil and water. Most of these methods utilize GC but have been modified by the addition of a PID or FID (Potter 1989, p. 97). A generalization is that TPH I investigations use methods with GCs and PIDs or FIDs and TPH II investigations often follow extraction by direct injection into a GC (Chang 1992, p. 240).

A PID is a nonspecific detector that measures total ionazable compounds, both organic and inorganic. Vapor phase compounds are drawn though a probe into an ionization chamber with windows through which an ultraviolet (UV) lamp emits photons with a specific energy (different bulbs = different energies). Molecules having lower ionization potentials than the radiated photon potentials will absorb a photon and become ionized ($AB + \text{photon} >> AB^{+} + e^{-}$). There are two electrodes to which a voltage is applied and the increase in current is proportional to the concentration of ionized molecules in the vapor phase.

The PID is not a destructive detector; the molecules exit the detector chemically unaltered from their original state. In general, the lower the ionization potential, the greater the PID's response to it. The response generally increases with increasing carbon numbers. The response increase with increasing unsaturation: benzene > cyclohexene > cyclohexane. Sensitivity for different types of petroleum hydrocarbons: aromatics > alkenes > alkanes and cyclic compounds > noncyclic compounds (Denahan 1990, p. 96).

FID is a nonspecific detector designed to measure total organic compounds present in the vapor phase. Vapor phase components are drawn through a probe into an

ionization chamber containing an oxygen-hydrogen flame where chem-ionization of the organic molecules occurs (CH + O >> CHO + e^-). The ions and electrons pass between electrodes to which voltage is applied, decreasing the resistance and causing a current to flow in the external circuit.

The FID responds to all organic molecules containing carbon atoms. In general, the detector's response will very slightly increase with increasing carbon number. It will be the relatively the same for alkanes, alkenes, and aromatics with the same number of carbon atoms (Denahan 1990, p. 95).

Calibration is extremely important to both the FID and PID. They respond quantitatively only to the individual compound for which they are calibrated. Response to unknowns can only be nonqualitative and semiquantitative. Additionally, the choice of target compound is important. If calibrated to a single carbon compound for which the detector is not very sensitive, the effect will be to make the detector significantly more sensitive. If calibrating the detector to a compound in the middle range of sensitivity, it will be less sensitive.

EPA 500, 600, and 8000 methods may be categorized as either a "volatiles" or a "semivolatiles" method depending on the relative volatility of their target compounds. This approach optimizes chromatographic separation, sample preconcentration, and injection techniques for the methods.

4.4.1 VOLATILE METHODS

"Volatiles" methods define volatiles as those compounds which can be effectively recovered from soil or water using "purge and trap" techniques. This involves purging the sample with an inert gas at room temperature and trapping volatile compounds stripped from the sample with a porous polymer adsorbent. The trapped compounds are desorbed directly into the inlet of a gas chromatograph by rapidly heating the trap after the column carrier gas has been diverted to flow through it.

Volatile methods include EPA Methods 602, 503.1, 8020, 524.1, 624, and 8240. These methods are routinely used to investigate gasoline releases (Potter 1989, p. 101). Volatile methods are effective for BTEX monitoring but are not applicable to the entire range of compounds found in petroleum products. The heavier range of these products are in the semivolatiles range.

Chang (1992) found that analysis using purge and trap techniques described above at elevated temperature of 85^{0}C was the best method for kerosene and diesel. The method is very reliable, sensitive, time-saving, and can detect volatile organics down to ppb or lower levels (p. 240).

4.4.2 SEMIVOLATILE METHODS

Higher boiling point "semivolatile" compound methods have alternate chromatographic and sample preconcentration techniques. These methods involve liquid/liquid and liquid/solid extraction with accompanying pH adjustment for recovery of "acidic" and "base/neutral" compounds. Some extracts are concentrated and injected

directly into the gas chromagraphs. Keith (1988) found that these acid and base/neutral extracts provide a much better measure of the level of soil contamination than any of the volatiles methods (p. 414).

EPA Methods 610, 625, 8250, and 8270 are more common "semivolatiles" methods. They are normally used for diesel fuels, kerosene, and #2 fuel oil and target key compounds such as napthalene and phenanthrene. Just as "volatiles" methods are not applicable to all compounds (heavy distillate range), "semivolatiles" methods are not applicable to all compounds in the middle distillate range like diesel fuel. Considering this when using this approach, it is best and appropriate in most circumstances to analyze samples for both volatiles and semivolatiles regardless of the product type.

4.4.3 ADVANTAGES AND DISADVANTAGES

EPA Methods were designed for target compounds (such as the 600 series for detection of compounds on the list of "priority pollutants") and divided into the categories of "volatiles" and "semivolatiles" as explained above. The problems encountered with this approach include detection of nontarget compounds and the limited range of methods relative to composition of the various products.

The use of CG with PID or FID has provided a tool for laboratories to improve upon EPA methods of measuring petroleum products and individual hydrocarbons in soils. These modified GC/FID or PID methods are a clear advancement over target compound methods because they provide more information that can be used to characterize the hydrocarbon products and quantify the concentrations (Douglas et al.

1992, p. 200). Without chromatographic separation, PID or FID methods are limited to the analysis of a known contaminant or contaminant mixture.

A disadvantage of the methods using GC is the fact that most compounds in heavy distillate products like motor oils and residual fuels are not amenable to analysis by GC. This is why more TPH III investigations are done gravimetrically.

4.5 PID V. FID

Since the use of PIDs and FIDs has been discussed above, it is important to show the differences in their capabilities and performance (Fizgerald 1988, p.125):

- The FID can detect methane while the PID cannot. Therefore, there is a possibility of misleading soil "hits" from natural methane conditions with the FID.
- The FID destroys the sample. This could be considered undesirable when repeat or simultaneous analysis of a sample by multiple techniques is desired.
- There is a significantly different response and selectivity between the two instruments. The PID is generally more sensitive to petroleum compounds than the FID. The FID response is roughly uniform for most volatile hydrocarbons. The PID response increases with the degree of unsaturation.
- The instrument flow rates and response characteristics vary. This is especially true when attempting to analyze small sample containers.

Chapter 5

FIELD TECHNIQUES

5.1 INTRODUCTION

Regulators have limited the use of field screening in lieu of laboratory analysis, in part, because there is little information on the accuracy and precision of field screening techniques. There has been growing favor with field screening or testing due to recent studies of their capabilities. Portable analytical units are becoming more efficient and widely used to investigate and document conditions of environmental contamination by complex mixtures such as those in petroleum distillates.

This chapter discusses the advantages of field testing as well as a few of the more commonly used field or on-site techniques for petroleum contamination investigations. Most of the recent study and research in the area of soils testing has occurred in the area of field testing. Therefore, there are many newer techniques than those covered within this chapter. This chapter will focus on those techniques more commonly used and accepted by the regulators, the following chapter will discuss a few more experimental techniques.

5.2 ADVANTAGES OF FIELD TESTING

The large number of advantages over laboratory testing continues to push field testing toward the front of petroleum investigations:

- Field screening consists of a number of techniques which are minimally intrusive but still require field efforts which costs an order of magnitude or more less than intrusive techniques such as soil borings or monitoring wells.
- The portable methods provide immediate, real-time data.
- The use of these techniques can more accurately guide the effective placement of monitoring wells, saving time and money.
- Consultants or contractors to have information on contamination while they work on a site, enabling them to make more accurate and timely decisions on the site.
- Field techniques may alleviate the loss of volatiles from samples that plagues the laboratory techniques.

5.3 FIELD GCs, PIDs, AND FIDs

Most of the portable field units used for field tests are designed to analyze gaseous samples at ambient temperatures. The field units developed have been basically GC, PID, and FID units redesigned to be taken to the field sites. The PIDs or FIDs can and have been used alone or in combination with a GC.

The FID or PID used alone can analyze soil gas utilizing the jar headspace technique as discussed in Chapter 3.3. The foil sealing the 1/2 full jars is punctured with the probe of a PID or FID and a reading is taken. The maximum response should occur within 2-5 seconds (Fizgerald 1989, p. 128). According to Klopp and Turriff (1994), this method is reasonably inaccurate and imprecise but is able to provide a ballpark

estimate. The FID is extremely sensitive to the contaminants present and the PID shows inconsistent bias of results which make concentration predictions difficult. It should not be considered an acceptable replacement for laboratory analysis (p. 143).

Ambient Screening is another field technique which utilizes only a PID or FID. It is the simplest method of collecting soil gas data and is very quick and inexpensive. As soils are removed from a bore hole, a detector is moved along the soil sample. Any positive response is recorded. The method provides real time information concerning the vertical distribution of contamination in the vadose zone. This method is easily influenced by variations in wind speed, moisture, and temperatures. It provides only general information about the soil and site (Denaham et al. 1990, p. 98).

As discussed in Chapter 3, the use of a GC with a PID or FID is a desirable method. With portable equipment, this technique can be brought to the field site. The soil gas can be obtained from a soil probe or jar headspace. Recommended procedures for gathering soil gas vary according to the manufacturers instructions but the basics are the same: it can be pulled by syringe from a probe sample bag or jar headspace. The combined GC with FID or PID provides more information on the contaminant than the PID or FID alone and is by far more accurate. It should be noted that GCs require a high degree of operator training and competence so may not be as easily used as the PID or FID alone (Klopp and Turriff 1994, p. 143).

Professor Gary Robbins of the University of Connecticut developed another field method of testing for petroleum contamination that utilizes an GC and a PID. The Lab in a Bag (LIAB) is a quart freezer bag employing a 3-way ball valve. It is attached

directly to a PID after stirring 25 mg of a soil sample with 100 mL of water within the bag with a magnetic stir. The remaining headspace is analyzed by a Photovac Snapshot GC to measure BTEX. Klopp and Turriff (1994) found LIAB to be extremely accurate but hindered by possible problems with contamination from sample to sample. Further investigation may prove this test quite viable (p. 143).

It should be noted that the GC with PID or FID has shortcomings. The equipment is mostly lab based instruments that aren't easily transportable and are expensive (both to buy and maintain). They are fairly delicate instruments than are not yet well adapted to field use. Depending on what equipment is utilized, it can demand a high level of training and proficiency.

5.4 IMMUNOASSAYS

Essentially, this technique uses characteristics of an immune system to detect petroleum products in soil. This relatively new technology relies on the very specific binding of animal derived proteins called antibodies with particular target molecules called antigens. The binding of the antibody to its target antigen forms the basis of the immunoassay. Their feasibility for analysis of petroleum contaminated soil has been demonstrated for numerous types of contaminants and petroleum products (Allen et al. 1992, p. 228).

A wide variety of immunoassay formats have been developed that range from simple "yes-no" screening assays to instrumental measurement. The specificity of the antibodies encourages the development of immunoassays for specific target compounds.

The majority of petroleum based immunoassays are designed for BTEX or TPH investigations.

Primary advantages of immunoassays include the high sensitivity, portability, and short analysis time. The high selectivity of the immunoassay permits crude sampling preparation. Additionally, the immunoassay procedures are much less expensive on a per sample basis than conventional methods (Vanderlaan et al. 1990, p. 29).

Disadvantages of immunoassays include the fact that many of the commercially available immunoassays only provide only a "yes-no" indication for results and that they require a high level of training and competence to obtain good results. Klopp and Turriff (1994) tested three commercial brands of immunoassays and found that they vary widely on accuracy, precision, and capabilities. The results obtained were considered slightly less accurate than jar headspace techniques (p. 143).

Chapter 6

PROTOTYPE FIELD TECHNIQUES

6.1 INTRODUCTION

This chapter provides an overview of the newer, somewhat experimental, techniques becoming available for petroleum product contamination investigations. Several of these techniques join older geophysical soil investigation techniques and equipment with newer analytical technology. The cone penetrometer, widely used for determining soil strength and type, is one of these geophysical techniques.

This is an appropriate place to explain the EPA's Monitoring and Measurement Technologies Program (MMTP). Its purpose is to accelerate the development, demonstration, and use of innovative monitoring, measurement, and characterization technologies at Superfund sites. Many of the field techniques mentioned in this report are being tested by various private organizations within the MMTP (U.S. EPA 1994).

6.2 LASER-INDUCED FLUORESCENCE

A pulsed laser fiber optic based fluorometer sensor system uses a hydraulic ram in a truck with a 20 ton reaction mass to push an instrumented probe into the ground. Flourescence is exited through a sapphire window in the probe by 337 nm light from a pulsed nitrogen laser. The excited pulse is transmitted down the probe over a silica clad optical fiber. The resulting flourescence from aromatic hydrocarbons in the soil is returned to the surface over a second fiber, dispersed with a spectrograph, and

quantified with an intensified linear photodiode array (Lieberman et al. 1992, p. 392). It provides real-time, in situ measurement of petroleum hydrocarbon contamination and soil type to depths of 50 m. Figure 2 is a schematic of a fiber optic fluorometer system with a cone penetrometer utilized to test for petroleum hydrocarbons.

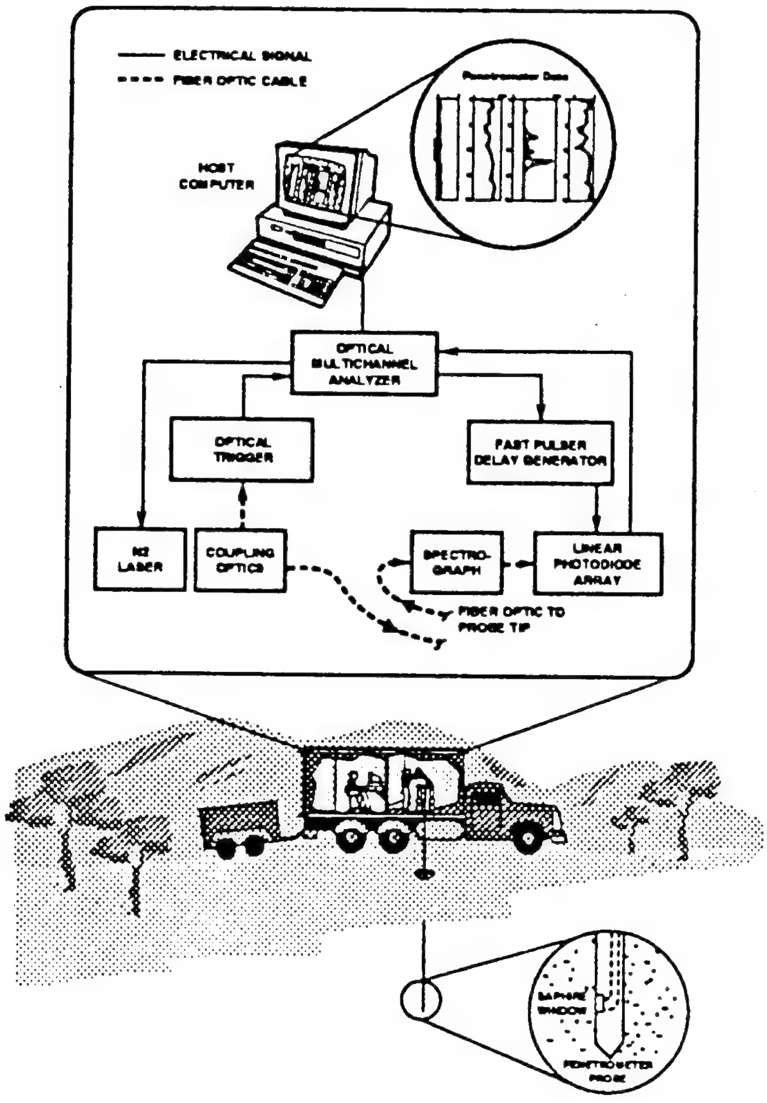


Figure 2: Schematic of Fiber Optic Fluorometer System
SOURCE: Lieberman et al. (1992)

Because this technique provides information on the soil type as well as the contaminant, it offers a multimedia approach to tracking the subsurface migration of the plume. The source of fluorescence in the petroleum products are the Polycyclic Aromatic Hydrocarbons (PAHs). There is evidence that petroleum products may be fingerprinted by the fluorescence spectral characteristics and lifetimes or their PAHs (Lieberman et al. 1992, p. 399). Additionally, unlike many laboratory testing techniques, there is no loss of the volatile components key to the contaminant.

Weaknesses of this technique include delicate lasers, the expense of the equipment, its maintenance, and brittle optic fibers. The optic fibers tend to attenuate in the UV region of the excitation beam (Dixon et al. 1990, p. 112).

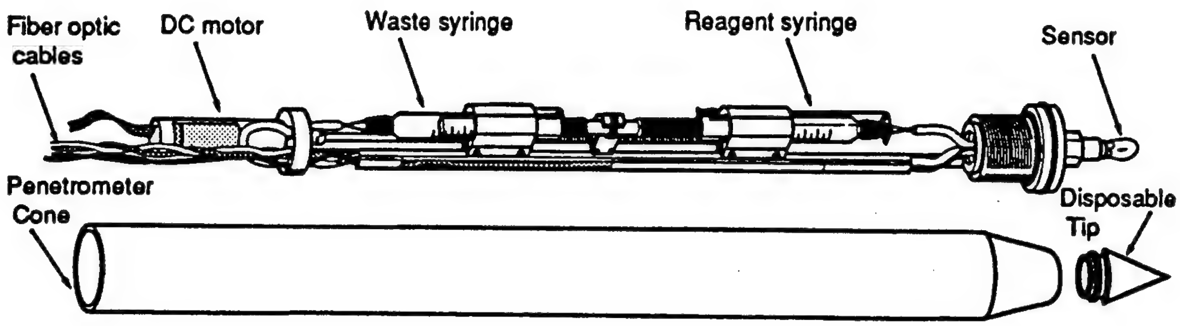
6.3 FIBER-OPTIC CHEMICAL SENSOR

This system utilizes optical fibers to monitor quantitative, irreversible chemical reactions that, upon exposure to various target molecules, form a product that absorbs visible light. The system delivers a reagent through a standard cone penetrometer system and monitors the colorimetric changes that occur. Figure 3 shows a typical assembly for this method. The reagent is connected to the sensor by micro-tubing. The syringe reservoirs can easily be removed for servicing and the cone is made from corrosion resistant steel tubing.

The fiber-optic chemical sensor has been evaluated against GC standards and its accuracy and sensitivity have been demonstrated sufficient for monitoring some

contaminants (Milanovich and Yow 1994, p. 139). It represents a rapid cost-effective means to obtain initial survey information of subsurface conditions.

Figure 3: Assembly Drawing of Reagent Delivery System and Penetrometer Cone.



SOURCE: Milanovich and Yow (1994)

Chapter 7

QUALITY ASSURANCE

7.1 INTRODUCTION

The reliability of data can be no greater than the reliability of the weakest part of the chain of events constituting the sampling and analysis. Certain principles of sampling, analysis, and quality assurance should prevail regardless of the variations experienced.

Quality assurance has two basic aspects (Keith 1988, p. 86):

1. Quality Control (QC) -- The application of good laboratory procedures, good measuring processes, and standard operating procedures (protocols).
2. Quality Assessment (QA) -- Monitoring for adherence to protocols.

This chapter provides some basic information sources of variability and quality assurance measures.

7.2 SOIL SAMPLING VARIABILITY

In any soil sampling program, variability can come from three basic sources:

1. The heterogeneity of the soil.
2. The adequacy of the samples in representing the population.
3. The accuracy of the sampling and analysis methods.

The problems of soil heterogeneity and representing the population can ideally be lessened by taking a multitude of samples. The mean and range of values are generally

better defined with a larger number of samples. Unfortunately, cost and technical considerations make the collection of large numbers of samples an unacceptable choice.

The sampling plan is where the problems of overcoming heterogeneity and representing the population is tackled. Intuitive sampling plans based on judgment and statistically based plans are the two ends of the spectrum of choice on sampling plans. Utilizing aspects of statistical analysis and intuition in a hybrid plan is the most commonly used approach. The only way to assure quality for the plan and its ability to overcome the problems of heterogeneity and representativeness is to review the plan's assumptions and statistical analysis.

A key to maintaining control over a sampling program is properly accounting for the samples. Part of that process relies on a solid system of marking samples. Due to the fact that soil is a continuous medium, it is necessary to put extra emphasis on the sample unit and location. Often it is helpful to put a 3-dimensional (volume, shape, and orientation) as well as a specific location on the sample unit (Barth et al. 1989, p. 2).

7.3 EVALUATING QUALITY ASSURANCE

Any measurement program should have built-in checks, applied by project personnel, to control data quality. Quality assurance is a difficult portion of any measuring program. The quality assessment portion is not extremely difficult as it is a matter of proper training, adherence to established standard operating procedures at all times, and periodic checks to ensure compliance. Spot checks of sampling methods, techniques, calculations, and data transcription can support quality assessment needs.

The quality control is more difficult due to subjectivity and a general lack of knowledge. The state of affairs in the domain of QC is somewhat in disarray. Multiple definitions exist for fundamentals such as bias, detection limits and even QC samples (Keith 1989, p. 84).

The EPA has developed a process which requires five data quality indicators (DQIs) to demonstrate quality assurance. These DQIs (precision, bias, representativeness, completeness, and comparability) provide a guideline for developing a quality assurance plan as well as for evaluating the quality of data. There are preferred procedures for assessing each indicator but some are not always applicable due to technology or resource constraints.

Precision is defined by the EPA as a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Three indications of precision may be obtained from the quality assurance program: the standard deviation of the actual reported values, the analysis of collocated or field-replicated samples, or the analysis of laboratory-replicated samples or repeated measurements of field samples spiked in the laboratory with the target analyte. Collection and analysis of collocated samples is the preferred procedure for estimating the precision of a measurement system. Collocated samples are two or more portions collected at the same point in time and space as to be considered the same (Keith 1988, p. 159).

Bias is the degree of agreement of a measurement and a reference or true value. Two bias terms can result from the quality assurance program: the bias based on the

analysis of field spiked samples or reference materials and the bias obtained from the repeated analyses of field samples or reference materials. The preferred measure of bias is the difference between the average measured value and the true value. Percent recovery is also frequently used in environmental measurement programs.

Representativeness is the correspondence between the analytical result and the actual environmental conditions. It can only be estimated because the "truth" is not known. It is assured by the random sampling from the target population. This can only be shown by description of the sampling plan, backing it with statistical calculations and experience.

Completeness is a measure of the amount of valid data obtained from the measurement system compared to what was expected to be obtained. There are calculations available to show a numerical value for completeness (Keith 1988, p. 167). How and why missing data is lost should be explained.

Comparability is the confidence with which the data can be compared to another set of data. Show how the data measured, its quality, and the measurement methods are comparable. Reasons should be given to back these claims.

The QA/QC section in a report should address those indicators of the DQIs above that are applicable. This enables the data user to properly assess the quality and accuracy of the data provided. It is desirable to see summarized tables of validated quality assurance data in a report. This allows the user to verify the reported results as well as begin to build a body of quality assurance data which will allow for comparisons to be make among studies. The reporter of the data should put special emphasis on the

levels of overall confidence and precision. If portions of the results are ambiguous and conclusions can not be supported by the data, the report should say so (Barth et al. 1989, p. 4).

Chapter 8

CASE STUDIES

8.1 INTRODUCTION

This chapter reviews data from two soil investigations that took place under the direction of EDE. The investigations are the product of two contracted organizations that conducted the studies and provided the data to EDE. Since both investigations are of a follow-up nature and are parts of larger, ongoing studies, this chapter concentrates on the data provided and not on decisions or recommendations that occurred before or as a result of them. It discusses the sampling methods, the analytical techniques used, and aspects of the Quality Assurance in each study. This chapter utilizes information provided within this report to provide insight about the investigation and its data.

The investigations provide different approaches to testing for petroleum product contamination that are covered within this report. The Hardstand #72 investigation utilized analytical laboratory and field techniques and the Oil Loading Station investigation utilized what is basically a field screening technique.

8.2 HARDSTAND #72

The purpose of this investigation was to complete previous investigations by establishing definite limits of the lateral and vertical extent of known petroleum product contamination and to investigate a section of the hardstand that had not yet been investigated. Earlier investigations had determined severe petroleum product

contamination in the southern areas of the hardstand. It was conducted in three phases with each phase further delineating the contamination and indicating whether the contaminated areas were connected or unique.

The extent of this investigation was determined within the work plan which was coordinated with EDE and in compliance with Wasserwirschaftsamt (Water Authority) Regensburg. The necessary drilling sites were for the most part determined in agreement with EDE after the first and second phases. Appendix A is a detailed representation of the site. The main focus was the areas surrounding the grease rack as well as the newly constructed waste oil collection building. The area to the northwest of building 1271 was not previously investigated. Test drillings were also performed in this open area. The investigation data is contained in Appendix B.

8.2.1. SAMPLING

HYDRODATA GmbH utilized percussion driven Sondier boring with a diameter of 50 mm to depths varying from 1.9 to 6.0 m to collect the soil samples. Immediately after extracting the drill stems, the drill core was homogenized and sampled a 1 m intervals. When the drilling could not reach the scheduled end-depth, the lowest sampling section was less than one meter. The total of 173 boring meters resulted in 179 samples. The samples were filled into 1000 mL glass bottles and stored in a cool, dark place for not more than 48 hours until they were transferred to the laboratories. The sampling containers were marked with stickers which had the sampling location, date, and depth clearly indicated.

The sampling was done by HYDRODATA and the samples were sent to two different laboratories for analysis. Figure 4 depicts the distribution of the samples and which laboratories they went to. Samples were handled in the same manner when delivered to the laboratories.

As stated in Chapter 3.2, the tool used for sampling is not really of concern as long as it is used uniformly with all samples. There was little chance of problems in this investigation, but the report should have explained the methods utilized.

The term "homogenized" was not specifically explained within the report. This could be an area of concern. It implies mixing and if this was the case, the integrity of the samples could have been compromised. At a minimum, volatile components of the samples may have been lost.

The time period between sampling and analysis may also be an area of concern. Although no more than 48 hours in a cool area was what the report stated, the exact definition of cool and the time to analysis was not specified. A temperature above the standard temperature of ice, and different transportation times to the laboratories may have been the reason behind differences in measured values. Effects of biodegradation and chemical oxidation due to temperature and time to analysis could have created inconsistencies. A closer examination and presentation of these factors would have been desirable to the user of the data.

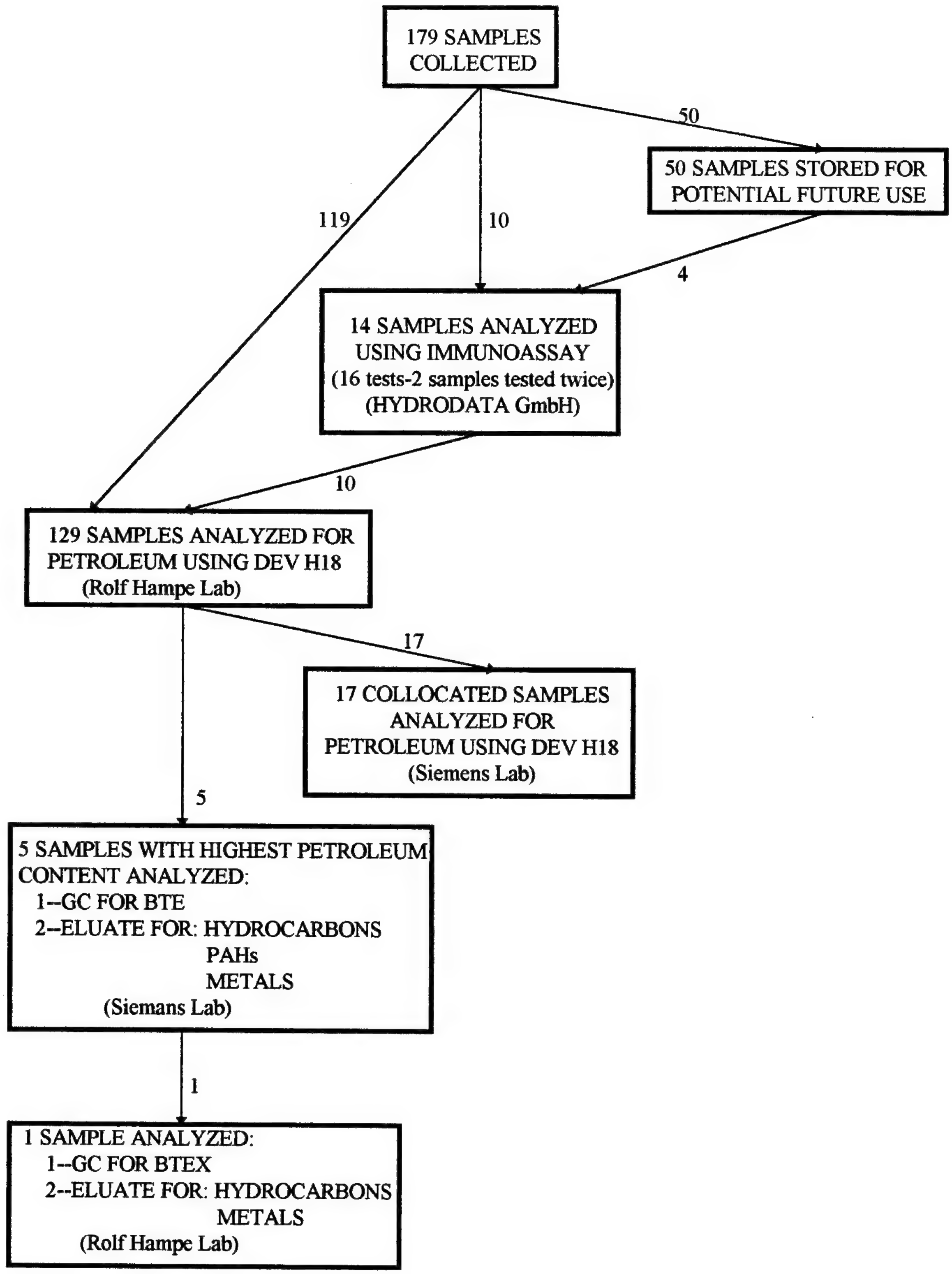


Figure 4: Flowchart of Samples and Analysis for Hardstand #72 Investigation.

8.2.2 ANALYTICAL METHODS

The range of analysis performed on the samples was determined in the schedule of services. Since petroleum product contamination was indicated within the previous investigations, the target compounds were known. HYDRODATA utilized the following tests and methods to analyze the samples:

146 Deutsche Einheits-Verfahren (DEV) H18 analysis for petroleum products

16 Immunoassays

6 GC analysis

6 Eluate analysis for hydrocarbons and metals

5 Eluate analysis for PAHs

The DEV H18 test is an infrared adsorption test similar to that utilized in EPA Method 418.1 discussed in Chapter 4 of this report. It is important to realize that with this technique, the weathering of the sample may greatly impact on the data obtained. There is also a possibility of a loss of volatiles during the solvent concentration step of this procedure. Also, there is the problem of heavier petroleum products being poorly soluble in the freon. This technique may lead to low values for concentrations.

HYDRODATA utilized the immunoassays as a field technique. The report indicated a lack of experience with this method when it discussed the problem of holding back the sampling process to conduct the immunoassays. This may be a source of problems with the data obtained from these tests. As discussed in Chapter 5 of this report, there is a need for good training and competence to obtain good results with immunoassays. Additionally, the immunoassay chosen for use delivered only range

indications for results. This makes comparison with other test results, which is what appeared to be HYDRODATA's goal, difficult and inconclusive.

The five samples with the highest petroleum product content were analyzed with a GC. No indication of any other method or detection instrument utilized with the GC was indicated. The GC separates the components of the sample, providing a good overview of the compounds within the contaminated soil. Concerns with this analysis should be the fact that the GC wasn't done until the results of the DEV H18 tests were run. In addition to the volatile losses and sample contamination possibilities from the sampling process, there was possible losses from the tests run for DEV H18. The results of the GC should be considered biased due to this fact.

The final method of analysis utilized was the mixture of an eluate and subsequent testing for total hydrocarbons using DEV H18 method for the five samples indicating the highest petroleum product content from the initial DEV H18 tests. The eluate is basically a dilution of the soil and its contaminants to test the leaching properties. The basic chemical composition of the soil is not changed. The same concerns with losses as indicated above should be considered with the data from these tests.

8.2.3. QUALITY ASSURANCE

HYDRODATA utilized three basic techniques to assure the quality of their data. They utilized two laboratories to analyze samples, they utilized collocated samples, and they repeatedly tested some samples. The following is a summary of the testing done for quality assurance and Figure 4 can assist in understanding the flow of these tests:

- 17 collocated samples of the 129 tested for DEV H18 were sent to a different laboratory and tested utilizing the same procedures. Additionally, these 17 samples were repeatedly tested by one of the laboratories.
- 1 of the 5 highest petroleum content samples tested utilizing the GC and eluate was sent to a different laboratory and tested utilizing the same procedures.
- 10 of the immunoassays were performed on samples in the field that later underwent DEV H18 analysis in the laboratory. 2 other samples were analyzed twice using the immunoassay.

HYDRODATA presented the data from the 17 Quality Assurance samples as shown in Table 4. A comparison of the immunoassay results and the main DEV H18 results was displayed in Table 5. In addition, the data is displayed as part of the larger presentation in Appendix B. For both comparisons, HYDRODATA found the results to be generally in agreement. They attributed the variations in DEV H18 test results to the homogeneity of the soil and the discrepancies in the immunoassay and DEV H18 data to the fact that the immunoassay is a somewhat new and, in this particular test, semi-quantitative method.

Utilizing the DQIs to analyze this investigation's data uncovers several potential areas for concern:

- Precision -- Collocated samples were utilized but the agreement in the results is not as good as HYDRODATA states. The time between sampling and analysis of the two different laboratories may have some impact on this.

Additionally, there may be some minor differences in the equipment or protocols at the two laboratories. The repeated sampling of the 17 samples chosen for quality assurance was not a good indicator of precision. No samples were spiked so there was no basis for comparison. Additionally, the results of these repeated tests was never presented by HYDRODATA.

Table 4: Comparison of QA Samples; Hardstand #72 Investigation

Sample	POL-Content Main Laboratory [ppm]	POL-Content QA/QC-Laboratory [ppm]	Remarks
HS72-52 BP1	37	190	*QA/QC-record higher*
HS72-56 BP2	19	< 2	*similar result*
HS72-58 BP2	540	< 2	*QA/QC-record lower*
HS72-62 BP2	16	< 2	*similar result*
HS72-67 BP1	970	110	*QA/QC-record lower*
HS72-68 BP2	360	630	*similar result*
HS72-70 BP3	26	< 2	*similar result*
HS72-74 BP3	15	17	*same result*
HS72-75 BP3	38	29	*same result*
HS72-77 BP1	138	5	*QA/QC-record lower*
HS72-81 BP5	91	10	*similar result*
HS72-88 BP1	348	930	*QA/QC-record higher*
HS72-89 BP2	48	14	*similar result*
HS72-94 BP3	21	180	*QA/QC-record higher*
HS72-96 BP2	20	6	*similar result*
HS72-100 BP3	8050	2500	*QA/QC-record lower*
HS72-103 BP2	1080	510	*QA/QC-record lower*

SOURCE: HYDRODATA GmbH (1995)

- Bias -- Was not mentioned within the investigation report. Again, there were no spiked samples analyzed for a basis for bias. The repeated testing of the

17 DEV H18 Quality Assurance samples was not presented or discussed with respect to possible bias.

Table 5: Comparison of Immunoassay Results; Hardstand #72 Investigation

Sample	Range of Concentration Dräger Envicheck KW [ppm]	POL Content Main Laboratory [ppm]	Remarks
HS72-58 BP1	> 1000	3050	*Indication correct*
HS72-58 BP4	< 100	16	*Indication correct*
HS72-65 BP2	< 100	32	*Indication correct*
HS72-69 BP2	< 100	77	*Indication correct*
HS72-69 BP5	< 100	n.a.	*Indication assumably correct*
HS72-71 BP2	100 - 1000	5400	*Indication incorrect (too low)*
HS72-71 BP4	100 - 1000	3850	*Indication incorrect (too low)*
HS72-72 BP1	> 1000	5900	*Indication correct*
HS72-72 BP4	> 1000	2200	*Indication correct*
HS72-73 BP2	< 100	n.a.	*Indication assumably incorrect*
HS72-73 BP5	< 100	n.a.	*Indication assumably correct*
HS72-76 BP5	< 100	600	*Indication ~~assumably~~ incorrect*
HS72-79 BP1	< 100	26	*Indication correct*
HS72-79 BP3	< 100	n.a.	*Indication assumably correct*
HS72-79 BP1	< 100	26	*Indication correct*
HS72-79 BP3	< 100	n.a.	*Indication assumably correct*

n.a.: Residual Sample, not analyzed yet.

SOURCE: HYDRODATA GmbH (1995)

- Representativeness -- This is probably not applicable to this investigation. Since it was a follow-up, this DQI had been covered within the earlier reports indicating the levels of petroleum products in and around the hardstand.
- Completeness -- Not discussed within the report. Although no missing data was indicated, there should have been an explanation for the selection of the

50 samples stored for potential use: reasoning for selection, areas chosen, and numbers chosen. Comparing the immunoassay results on samples that were part of these 50 was not appropriate (see Table 5).

- Comparability -- Other than the immunoassay comparison, there was no mention of how the data presented compared to existing data. This was easy for the user to do by comparing data from the previous investigations of this area to what was presented but probably should have been provided by HYDRODATA.

8.3 PHASE III SOIL AND GROUNDWATER INVESTIGATION

The purpose of this investigation was to provide additional characterization of five sites located within the northeastern edge of the Grafenwohr Training Area. The portion of the investigation chosen for review in this report was Area 2, the Oil Loading Station (OLS). The main goal of the OLS investigation was to assess the extent and degree of lead in the soil in the area of the station. It also screened the soil for petroleum product contamination. The previous investigation had indicated levels of Pb above the Bavarian thresholds for remediation

The extent of this investigation was determined within the scope of work. Sampling plans and drilling locations were based mainly on discussions with the Wasserwirschaftsamt (water authority) Weiden. Appendix C is a detailed representation of the OLS site. . The soil was tested for petroleum contamination in addition to metals. The drilling locations were distributed so that the soil from underneath the concrete and

around the perimeter of the OLS could be sampled. The investigation data is contained in Appendix D.

8.3.1 SAMPLING

Soil samples were collected using a percussion drill with 36 mm diameter steel core barrels. There were 10 drillings of boreholes to a depth of 2 m. Composite samples were taken from each meter resulting in 20 total samples. Soil sampling was supervised by Dames & Moore. The investigation report does not include any specific description of the procedures for handling the samples. The schedule of services required that the samples be stored in sturdy, air-tight containers and maintained by the contractor until acceptance of the final report (Dames & Moore GmbH, 1995). The samples for petroleum product analysis were placed in 250 mL sample jars and screened by inserting a PID inlet tip into the jar. No other specifics regarding the sample preservation, storage, or transportation were given within the final report.

As discussed in Chapter 3.2, the specific tool used for gathering the sample is not likely a source of possible error as long as it was uniformly used. The report should contain some mention of what tool was utilized.

The term "composite samples" may give some reason for concern regarding the sampling process. It was not explained but implies that the soil was manipulated in some manner when it was taken from the core barrels. If the soil sample was mixed or disturbed in an excessive manner, the results of the petroleum contaminant screening may have been affected. This is especially true for any analysis of volatiles.

The fact that the report did not provide any specific information on how the samples were handled may also give some concern. Time of storage, temperature, and presence of headspace within the sample could affect results from analysis for petroleum products and should be explained in the report.

8.3.2 ANALYTICAL METHODS

The petroleum product testing in the OLS investigation was of a screening type. Samples were tested for petroleum vapors utilizing a PID. The results are in the third column of the Table in Appendix D. It should be noted that the THC (Total Hydrocarbon) column in this Table is for total hydrocarbon analysis by GC-MS on groundwater samples from monitoring wells (DM-7.1 & 7.2). They do not deal with soil samples from the OLS investigation.

The PID measurements provide a semi-qualitative assessment of organic vapors. Specification of the vapors is not possible with the PID alone but Dames & Moore GmbH assumed that the vapors were consistent with BTEX because they are commonly present in fuel oil which was already determined to be the main contaminant in the area.

The specific procedure for the PID screening was not discussed. There are procedures as discussed in Chapter 3.3 of this report which provide the best results. The results could have been affected by a number of procedural inconstancies:

- Sample jars not filled to 1/2 capacity.
- Not agitated and allowed to equilibrate for 5-10 seconds.
- Not properly sealing the jar until probed.

- The time between sample collection and screening.

As long as each test is run in an identical manner, these details may be minor and do little to the data obtained. If the procedures varied from sample to sample, they could cause large variances. Reviewing the data in Appendix D, there are two sample values with very high PID readings: OLS 3/2 and OLS 6/2. Without better explanation from Dames and Moore GmbH, the variations in the PID headspace procedure could be assumed to be responsible for them.

8.3.3 QUALITY ASSURANCE

Quality Assurance consisted of analyzing identical samples from the same location (collocated samples) for the same parameters. 10 % of samples collected were analyzed for Quality Assurance. The last two rows of data in Appendix D are from the collocated samples. Quality Control consisted of analyzing distilled groundwater run through the sampling equipment in order to check for false positives generated from the sampling equipment.

Utilizing the DQIs to analyze the investigation data:

- Precision -- Collocated samples were utilized. The results show relatively consistent results. Sample OLS 10/1 compares with OLS A as does OLS 10/2 with OLS B. These data would be better supported with a more thorough explanation of the procedures utilized during the PID screening.

- Bias -- The report did not discuss this aspect. No field spiked samples or reference materials were utilized and there was no mention of repeated analyses of field samples.
- Representativeness -- Not required in this investigation. This DQI should have been discussed in earlier investigations of this area to explain the differences between what was found in this area and the environmental conditions in the surrounding areas.
- Completeness -- Within the area of PID testing, there was no data that was missing or unexplained.
- Comparability -- There was no mention of the confidence in the PID data with reference to another set of data.

Chapter 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

All conclusion are those of the author. Both Dames and Moore GmbH and HYDRODATA GmbH investigations reported data that was used in part to arrive at the conclusions.

- Due to the complex nature of petroleum products, knowledge of the possible type of petroleum product contamination is vital to narrowing the choice of testing methods. Knowing what to look for (TPH I, II, III, volatiles, semivolatiles,...) greatly assists in choosing the appropriate test method. This is especially true with laboratory methods.
- Sample collection and preservation are important aspects of soil testing. For petroleum testing, time between sampling and testing, storage temperature, and storage itself can greatly affect data obtained. Procedures should be clearly stated and uniformly followed.
- Laboratory techniques of testing soils for petroleum contamination are diverse and often not well specified. The use of GC with MS, PIDs, or FIDs is the laboratory approach that provides the most thorough data.
- Field techniques of testing soils for petroleum contamination are not generally well accepted but continue to gain acceptance with further research. Portable laboratory equipment (GC, MS, PID, & FID) provide

results comparable to laboratory results with proper operation but are not yet completely durable or easily utilized in the field. Immunoassays provide good results with proper operation and understanding. Prototype field techniques are growing in utilization due in part to the EPA's Monitoring and Measurement Technologies Program.

- Quality assurance measures should be clearly and decisively planned and explained in any soil testing program. The utilization of Data Quality Indicators to plan and evaluate can create a more confidence in the data obtained.
- Both cases studied lacked details which left questions about data quality and accuracy. Specifications on sampling procedures, sample testing, and Quality Assurance measures were omitted.

9.2 RECOMMENDATIONS

1. Due to the emerging nature of technology utilized in the field of testing soils for petroleum contamination, every effort must be made to stay abreast of changes and developments. A professional development program should incorporate this area of study. The EPA's Monitoring and Measurements Technologies Program can assist in this area.
2. Schedules of services should require contractors to provide the following in soil investigation reports:

- Specific information regarding the sampling program to include time between sampling and testing, sample storage temperature, and presence (if any) of headspace in the sample containers.
- Specific information about testing procedures and order of tests (if there are more than one per sample).
- Outline of the quality assurance program utilizing the applicable five Data Quality Indicators as outlined by the EPA.

3. Utilize other soil investigation of a similar nature for comparison purposes. Continued examination and comparison should result in uncovering trends adding to those services requested from contractors.

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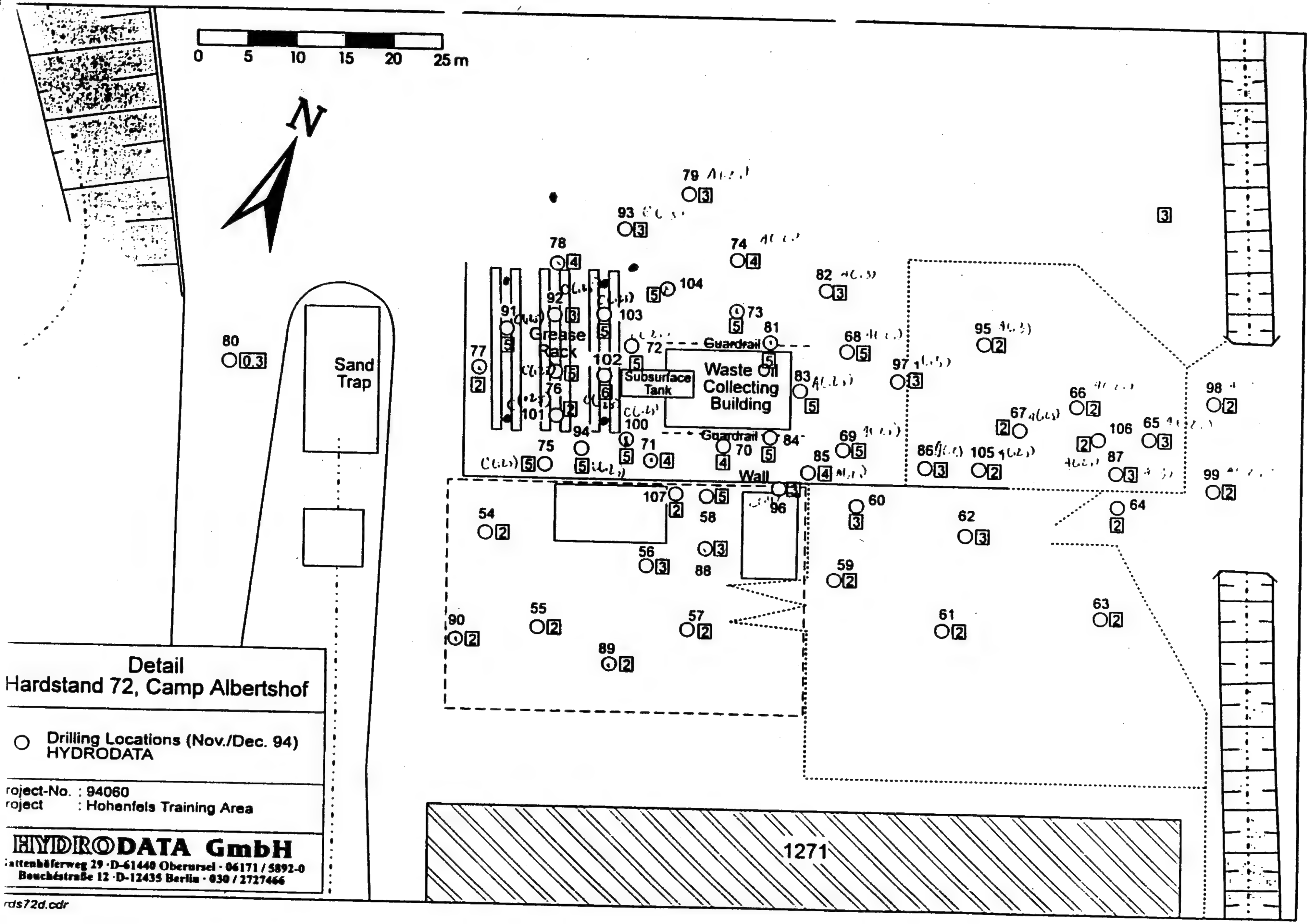
Appendix A

Detail from Hardstand #72 Investigation



Detail
Hardstand 72, Camp Albertshof

○ Drilling Locations (Nov./Dec. 94) HYDRODATA

roject-No. : 94060
roject : Hohenfels Training Area

HYDRODATA GmbH
attenhöferweg 29 · D-61440 Oberursel · 06171 / 5892-0
Bouchéstraße 12 · D-12435 Berlin · 030 / 2727466

rds72d.cdr

Appendix B

Data from Hardstand #72 Investigation

Laboratory Results - Site Survey and Remediation Design, Hohenfels

Project: Hardstand #72, Albertshof Sampling Date: Nov./Dec. 1994

Sample			Depth m		POL ppm	POL QA/QC ppm	POL Eluate ppm	Immuno-assay ppm
HS72-	54	BP1	0,35 - 1,0		37	190		
		BP2	1,0 - 2,0		10			
HS72-	55	BP1	0,35 - 1,0		38			
		BP2	1,0 - 2,0	R				
HS72-	56	BP1	0,35 - 1,0		21			
		BP2	1,0 - 2,0		19	< 2		
		BP3	2,0 - 3,0	R				
HS72-	57	BP1	0,35 - 1,0		19			
		BP2	1,0 - 2,0	R				
HS72-	58	BP1	0,35 - 1,0		3050			> 1000
		BP2	1,0 - 2,0		540	< 2		
		BP3	2,0 - 3,0	R				
		BP4	3,0 - 4,0		16			< 100
		BP5	4,0 - 5,0	R				
HS72-	59	BP1	0,25 - 1,4		10			
		BP2	1,4 - 2,0		38			
HS72-	60	BP1	0,25 - 0,9		14			
		BP2	0,9 - 2,0		22			
		BP3	2,0 - 2,5	R				
HS72-	61	BP1	0,25 - 1,1	R				
		BP2	1,1 - 2,0		11			
HS72-	62	BP1	0,25 - 0,9		11			
		BP2	0,9 - 2,0		16	< 2		
		BP3	2,0 - 3,0	R				
HS72-	63	BP1	0,25 - 1,1		17			
		BP2	1,1 - 2,0	R				
HS72-	64	BP1	0,25 - 1,1		78			
		BP2	1,1 - 2,0		11			
HS72-	65	BP1	0,25 - 0,8		3900			
		BP2	0,8 - 2,0		32			< 100
		BP3	2,0 - 3,0		52			
HS72-	66	BP1	0,25 - 1,0		97			
		BP2	1,0 - 2,0		32			
HS72-	67	BP1	0,25 - 1,0		970	110		
		BP2	1,0 - 2,0		330			

Laboratory Results - Site Survey and Remediation Design, Hohenfels

Project: Hardstand #72, Albertshof — **Sampling Date: Nov./Dec. 1994**

Sample			Depth m		POL ppm	POL QA/QC ppm	POL Eluate ppm	Immuno-assay ppm
HS72-	68	BP1	0,25 - 1,0		650			
		BP2	1,0 - 2,2		360	630		
		BP3	2,2 - 3,0	R				
		BP4	3,0 - 4,0		49			
		BP5	4,0 - 5,0	R				
HS72-	69	BP1	0,25 - 1,1		1650			
		BP2	1,1 - 1,9		77			< 100
		BP3	1,9 - 3,0	R				
		BP4	3,0 - 4,0		28			
		BP5	4,0 - 4,6	R				< 100
HS72-	70	BP1	0,0 - 1,0		270			
		BP2	1,0 - 2,2		4450			
		BP3	2,2 - 3,0		26	< 2		
		BP4	3,0 - 3,8	R				
HS72-	71	BP1	0,0 - 1,0		280			
		BP2	1,0 - 2,0		5400			100 - 1000
		BP3	2,0 - 3,1		4950			
		BP4	3,1 - 3,9		3850			100 - 1000
HS72-	72	BP1	0,25 - 1,0		5900		0.08	> 1000
		BP2	1,0 - 2,2		318			
		BP3	2,2 - 3,0		4150			
		BP4	3,0 - 4,0		2200			> 1000
		BP5	4,0 - 4,4		2600			
HS72-	73	BP1	0,0 - 1,0		200			
		BP2	1,0 - 2,0	R				< 100
		BP3	2,0 - 3,0		328			
		BP4	3,0 - 4,0		112			
		BP5	4,0 - 5,0	R				< 100
HS72-	74	BP1	0,25 - 1,0		360			
		BP2	1,0 - 2,0	R				
		BP3	2,0 - 3,0		15	17		
		BP4	3,0 - 3,4	R				
HS72-	75	BP1	0,25 - 1,0		360			
		BP2	1,0 - 2,0		135			
		BP3	2,0 - 3,0		38	29		
		BP4	3,0 - 4,0	R				
		BP5	4,0 - 4,6		10			
HS72-	76	BP1	0,25 - 1,0		3250			
		BP2	1,0 - 2,0		120			
		BP3	2,0 - 3,0		935			
		BP4	3,0 - 4,0		240			
		BP5	4,0 - 5,0		600			< 100

Laboratory Results - Site Survey and Remediation Design, Hohenfels

Project: Hardstand #72, Albertshof **Sampling Date: Nov./Dec. 1994**

Sample	Depth m	POL ppm	POL QA/QC ppm	POL Eluate ppm	Immuno- assay ppm
HS72- 77 BP1	0,0 - 1,0	138	5		
BP2	1,0 - 2,2	14			
HS72- 78 BP1	0,0 - 1,2	42			
BP2	1,2 - 2,0	21			
BP3	2,0 - 3,0	16			
BP4	3,0 - 3,5	R			
HS72- 79 BP1	0,25 - 1,0	26			< 100, < 100
BP2	1,0 - 2,0	24			
BP3	2,0 - 3,0	R			< 100, < 100
HS72- 80	0,0 - 0,3	R			
HS72- 81 BP1	0,0 - 1,0	44			
BP2	1,0 - 2,0	R			
BP3	2,0 - 3,0	315			
BP4	3,0 - 4,0	R			
BP5	4,0 - 5,0	91	10		
HS72- 82 BP1	0,3 - 1,0	1215			
BP2	1,0 - 2,0	45			
BP3	2,0 - 2,6	R			
HS72- 83 BP1	0,3 - 1,0	977			
BP2	1,0 - 2,0	40			
BP3	2,0 - 3,0	R			
BP4	3,0 - 4,0	R			
BP5	4,0 - 5,0	49			
HS72- 84 BP1	0,0 - 1,0	4500			
BP2	1,0 - 2,0	220			
BP3	2,0 - 3,0	R			
BP4	3,0 - 4,0	R			
BP5	4,0 - 5,0	64			
HS72- 85 BP1	0,3 - 1,0	450			
BP2	1,0 - 2,0	350			
BP3	2,0 - 3,0	R			
BP4	3,0 - 3,6	R			
HS72- 86 BP1	0,3 - 1,0	3400		< 0.02	
BP2	1,0 - 2,0	83			
BP3	2,0 - 3,0	R			
HS72- 87 BP1	0,3 - 1,0	960			
BP2	1,0 - 2,0	18			
BP3	2,0 - 3,0	R			

Laboratory Results - Site Survey and Remediation Design, Hohenfels
Project: Hardstand #72, Albertshof Sampling Date: Nov./Dec. 1994

Sample			Depth m	POL ppm	POL QA/QC ppm	POL Eluate ppm	Immuno-assay ppm
HS72-	88	BP1	0,0 - 1,0	348	930		
		BP2	1,0 - 2,0	71			
		BP3	2,0 - 3,0	R			
HS72-	89	BP1	0,0 - 1,0	700			
		BP2	1,0 - 2,0	48	14		
HS72-	90	BP1	0,0 - 1,0	2900			
		BP2	1,0 - 1,9	525			
HS72-	91	BP1	0,25 - 1,0	930			
		BP2	1,0 - 2,0	138			
		BP3	2,0 - 3,0	R			
		BP4	3,0 - 4,0	R			
		BP5	4,0 - 5,0	< 5			
HS72-	92	BP1	0,25 - 1,0	620			
		BP2	1,0 - 2,0	32			
		BP3	2,0 - 2,55	R			
HS72-	93	BP1	0,3 - 1,0	31			
		BP2	1,0 - 2,0	R			
		BP3	2,0 - 2,8	R			
HS72-	94	BP1	0,3 - 1,0	3186			
		BP2	1,0 - 2,0	405			
		BP3	2,0 - 3,0	21	180		
		BP4	3,0 - 4,0	R			
		BP5	4,0 - 4,8	13			
HS72-	95	BP1	0,3 - 1,0	590			
		BP2	1,0 - 2,0	R			
HS72-	96	BP1	0,35 - 1,0	17			
		BP2	1,0 - 2,0	20	6		
		BP3	2,0 - 3,0	R			
HS72-	97	BP1	0,3 - 1,0	1531			
		BP2	1,0 - 2,0	40			
		BP3	2,0 - 3,0	R			
HS72-	98	BP1	0,25 - 1,0	45			
		BP2	1,0 - 2,0	R			
HS72-	99	BP1	0,25 - 1,0	45			
		BP2	1,0 - 2,0	R			
HS72-	100	BP1	0,25 - 1,0	3600			
		BP2	1,0 - 2,0	330			
		BP3	2,0 - 3,0	8050	2500	0.06	

Laboratory Results - Site Survey and Remediation Design, Hohenfels

Project: Hardstand #72, Albertshof Sampling Date: Nov./Dec. 1994

Sample		Depth m		POL ppm	POL QA/QC ppm	POL Eluate ppm	Immuno-assay ppm
	BP4	3,0 - 4,0		3100			
	BP5	4,0 - 4,3		405			
HS72- 101	BP1	0,25 - 1,0		7500		< 0.02	
	BP2	1,0 - 2,0		3500			
HS72- 102	BP1	0,25 - 1,0		12500		0.07, < 0.05	
	BP2	1,0 - 2,0		2400			
	BP3	2,0 - 3,0		750			
	BP4	3,0 - 4,0	R				
	BP5	4,0 - 5,0		280			
	BP6	5,0 - 6,0	R				
HS72- 103	BP1	0,25 - 1,0		5500			
	BP2	1,0 - 2,0		1080	510		
	BP3	2,0 - 3,0		250			
	BP4	3,0 - 4,0	R				
	BP5	4,0 - 5,0		235			
HS72- 104	BP1	0 - 1,0		690			
	BP2	1,0 - 2,0	R				
	BP3	2,0 - 3,0		700			
	BP4	3,0 - 4,0	R				
	BP5	4,0 - 4,8		89			
HS72- 105	BP1	0,25 - 1,0		480			
	BP2	1,0 - 2,0		43			
HS72- 106	BP1	0,25 - 1,0		90			
	BP2	1,0 - 2,0		78			
HS72- 107	BP1	0,35 - 1,0		110			
	BP2	1,0 - 2,0		120			
Detection Limits				5	2	0.02	--

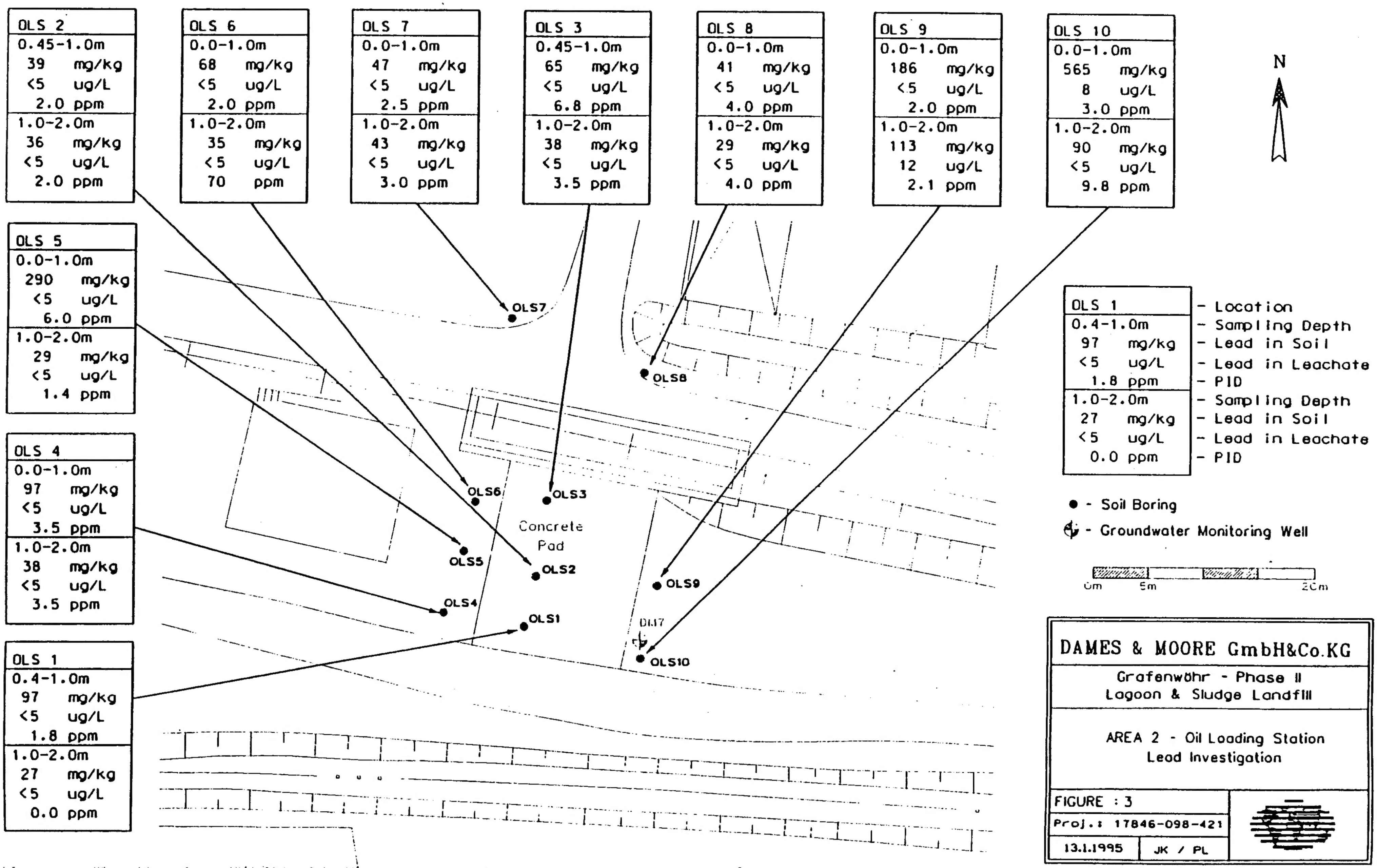
R = Residual Samples, stored for potential further analyses

(light shading) = POL-Concentration 1000 ppm to 5000 ppm

(dark shading) = POL-Concentration >5000 ppm

Appendix C

Detail of Oil Loading Station Investigation



OLS 2
0.45-1.0m
39 mg/kg
<5 ug/L
2.0 ppm
1.0-2.0m
36 mg/kg
<5 ug/L
2.0 ppm
OLS 6
0.0-1.0m
68 mg/kg
<5 ug/L
2.0 ppm
1.0-2.0m
35 mg/kg
<5 ug/L
70 ppm
OLS 7
0.0-1.0m
47 mg/kg
<5 ug/L
2.5 ppm
1.0-2.0m
43 mg/kg
<5 ug/L
3.0 ppm
OLS 3
0.45-1.0m
65 mg/kg
<5 ug/L
6.8 ppm
1.0-2.0m
38 mg/kg
<5 ug/L
3.5 ppm
OLS 8
0.0-1.0m
41 mg/kg
<5 ug/L
4.0 ppm
1.0-2.0m
29 mg/kg
<5 ug/L
4.0 ppm
OLS 9
0.0-1.0m
186 mg/kg
<5 ug/L
2.0 ppm
1.0-2.0m
113 mg/kg
12 ug/L
2.1 ppm
OLS 10
0.0-1.0m
565 mg/kg
8 ug/L
3.0 ppm
1.0-2.0m
90 mg/kg
<5 ug/L
9.8 ppm
N
OLS 5
0.0-1.0m
290 mg/kg
<5 ug/L
6.0 ppm
1.0-2.0m
29 mg/kg
<5 ug/L
1.4 ppm
OLS 4
0.0-1.0m
97 mg/kg
<5 ug/L
3.5 ppm
1.0-2.0m
38 mg/kg
<5 ug/L
3.5 ppm
OLS 1
0.4-1.0m
97 mg/kg
<5 ug/L
1.8 ppm
1.0-2.0m
27 mg/kg
<5 ug/L
0.0 ppm
OLS7
OLS8
OLS6
OLS3
Concrete Pad
OLS5
OLS2
OLS9
OLS4
OLS1
DH7
OLS10
OLS 1 - Location
0.4-1.0m - Sampling Depth
97 mg/kg - Lead in Soil
<5 ug/L - Lead in Leachate
1.8 ppm - PID
1.0-2.0m - Sampling Depth
27 mg/kg - Lead in Soil
<5 ug/L - Lead in Leachate
0.0 ppm - PID
● - Soil Boring
- Groundwater Monitoring Well
0m
5m
20m
DAMES & MOORE GmbH&Co.KG
Grafenwöhr - Phase II
Lagoon & Sludge Landfill
AREA 2 - Oil Loading Station
Lead Investigation
FIGURE : 3
Proj.: 17846-098-421
13.1.1995
JK / PL

Appendix D

Data from Oil Loading Station Investigation

Table 7.1: Soil Results, Area 2 (Oil Loading Station). (All results in mg/kg unless noted)

Guideline	Sample Depth (m)	PID (ppm)	THC	Phenol, Index	Pb	Cu	Cr	Cd	Ni	Hg	Zn	As	Dry Residue	Residue on Ignition
LfW-1			1000	1	150	100	250	5	100	2	500	30		
LfW-2			5000	10	600	500	800	20	500	10	3000	50		
DM7.1	0.0 - 1.0		<2	<0.1	620	13	6	0.1	5	<0.1	50	2	91.9%	98.7%
DM7.2	1.0 - 1.7		43	<0.1	110	8	7	0.2	7	<0.1	37	2	85.6%	98.9%
OLS 1/1	0.4 - 1.0	1.8	n.a.	n.a.	97	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 1/2	1.0 - 2.0	0.0	n.a.	n.a.	27	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 2/1	0.45 - 1.0	2.0	n.a.	n.a.	39	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 2/2	1.0 - 2.0	2.0	n.a.	n.a.	36	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 3/1	0.45 - 1.0	6.8	n.a.	n.a.	65	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 3/2	1.0 - 2.0	35	n.a.	n.a.	38	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 4/1	0.0 - 1.0	3.5	n.a.	n.a.	97	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 4/2	1.0 - 2.0	3.5	n.a.	n.a.	38	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 5/1	0.0 - 1.0	6.0	n.a.	n.a.	290	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 5/2	1.0 - 2.0	1.4	n.a.	n.a.	29	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 6/1	0.0 - 1.0	2.0	n.a.	n.a.	68	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 6/2	1.0 - 2.0	70	n.a.	n.a.	35	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 7/1	0.0 - 1.0	2.5	n.a.	n.a.	47	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 7/2	1.0 - 2.0	3.0	n.a.	n.a.	43	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table 7.1: Soil Results, Area 2 (Oil Loading Station). (All results in mg/kg unless noted)

Guideline	Sample Depth (m)	PID (ppm)	THC	Phenol, Index	Pb	Cu	Cr	Cd	Ni	Hg	Zn	As	Dry Residue	Residue on Ignition
LfW-1			1000	1	150	100	250	5	100	2	500	30		
LfW-2			5000	10	600	500	800	20	500	10	3000	50		
OLS 8/1	0.0 - 1.0	4.0	n.a.	n.a.	41	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 8/2	1.0 - 2.0	4.0	n.a.	n.a.	29	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 9/1	0.0 - 1.0	2.0	n.a.	n.a.	186	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 9/2	1.0 - 2.0	2.1	n.a.	n.a.	113	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 10/1	0.0 - 1.0	3.0	n.a.	n.a.	565	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OLS 10/2	1.0 - 2.0	9.8	n.a.	n.a.	90	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OSL A (QA, OLS 10/1)	0.0 - 1.0	5.5	n.a.	n.a.	760	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
OSL B (QA, OLS 10/2)	1.0 - 2.0	7	n.a.	n.a.	146	n.a.	n.a	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

DM7.1 / DM 7.2 : 9.Mar.94
OLS ... : 14.Dec.94